



# Tar abatement in a fixed bed catalytic filter candle during biomass gasification in a dual fluidized bed



F. García-Labiano<sup>a,\*</sup>, P. Gayán<sup>a</sup>, L.F. de Diego<sup>a</sup>, A. Abad<sup>a</sup>, T. Mendiara<sup>a</sup>, J. Adánez<sup>a</sup>,  
M. Nacken<sup>b</sup>, S. Heidenreich<sup>b</sup>

<sup>a</sup> Department of Energy and Environment, Instituto de Carboquímica (ICB-CSIC) Miguel Luesma Castán 4, 50018, Zaragoza, Spain

<sup>b</sup> Pall Filtersystems GmbH Production Site Schumacher, Zur Flügellau 70, 74564 Crailsheim, Germany

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## ABSTRACT

Catalytic filters are a novel technology for tar conversion in biomass gasification processes. Both particle elimination and tar abatement can be achieved in a single step at high temperatures minimizing energy efficiency penalties. This paper analyses the performance of a fixed bed catalytic filter candle in the reduction of biomass tar generated *in situ* in a dual fluidized bed gasifier (DFBG). In this study, the temperature of the filter was limited to 800 °C. Several variables affecting the performance of the filter were tested. Experiments at different gasification temperatures in the range 750–850 °C were performed so that the amount of tar reaching the catalytic filter was varied. The amount of tar at the catalytic filter inlet did not affect the tar conversion achieved which was around 75%. The major tar compound in the gasification gas at the outlet of the catalytic filter was naphthalene. At the highest temperature tested (850 °C), the tar content in the clean gas was 0.65 g/Nm<sup>3</sup>. The effect of the face velocity in the filter on the tar conversion reached was evaluated. Tar conversion decreased when the face velocity increased from 40 to 90 m/h as the residence time of the gas in the catalytic filter was lower. The ratio H<sub>2</sub>O to dry biomass was also varied (0.5–0.9) in order to produce tars of different nature. Higher conversions were achieved for higher values of this ratio.

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## 1. Introduction

Biomass as fuel represents an increasingly interesting option to decrease the CO<sub>2</sub> emissions associated to fossil fuel combustion. One of the possibilities is biomass gasification. Gasification is a thermal process in which biomass is converted to valuable gases, mainly H<sub>2</sub> and CO, in the presence of a gasifying agent (air, oxygen, steam, CO<sub>2</sub> or mixtures of these gases). Dual fluidized bed gasifiers (DFBGs) operated with steam as gasifying agent have demonstrated their advantages in terms of improving gasification efficiency and minimize the generation of by-products such as tar [1]. A dual fluidized bed gasifier consists of two separate reactor zones: a steam gasifier where biomass is converted to nitrogen-free syngas and a combustor where air oxidizes the residual char therefore providing the heat needed to gasify biomass. Typically, the gasifier is a bubbling fluidized bed (BFB) and the combustor is a circulating fluidized bed (CFB). Examples of operating plants are the 8 MW<sub>th</sub>

Güssing gasifier (Austria) [2] and the 2 MW<sub>th</sub> gasifier at Chalmers University of Technology [3].

Depending on the composition of the gasification gases, the product gas can be burned to produce heat, coupled to gas turbines or fuel cells to produce electrical power or used for the synthesis of hydrogen, methanol and liquid fuels [4]. However, during the gasification process tar appears as by-product of biomass conversion. Tar is defined as all organic compounds with a molecular weight larger than benzene [5]. The formation of tar represents one of the main drawbacks for the commercialization of this technology [6] as it can condense easily and therefore be the cause of downstream pipeline blocking and engine or turbine fouling. In order to become a competitive technology, tar concentration in the product gas of a biomass gasifier should be reduced to levels that can simultaneously comply with environmental regulations and be compatible with the end application [7]. Some indicative specifications for tar content in the gasification product gas can be found in literature. For gas engines, less than 50 mg/Nm<sup>3</sup> are required. In the case of fuel cells or syngas or methanol synthesis, the limits are quite lower, less than 1 and 0.1 mg/Nm<sup>3</sup>, respectively [6].

\* Corresponding author.

E-mail address: [glabiano@icb.csic.es](mailto:glabiano@icb.csic.es) (F. García-Labiano).

Tar abatement measures have been traditionally classified into two different categories: primary and secondary methods. A primary method implies tar reduction inside the gasifier bed while secondary methods include cleaning downstream the gasifier. As primary measure, non-metallic catalysts are added to the gasification bed to reduce *in situ* the tar produced in biomass gasification. Dolomites are the most widely in-bed catalysts for tar conversion in biomass gasification processes. Olivine, another naturally occurring mineral, has also demonstrated tar conversion activity similar to that of calcined dolomite and is a much more robust material than calcined dolomite. In a previous paper from the authors, a new developed Fe/olivine material [8] was tested as in-bed catalyst for tar conversion [9]. The capacity of this material for primary in-bed reduction of biomass tar in a dual fluidized bed system was assessed. The Fe/olivine material led to an important decrease in the amount of produced tar. As secondary measure, commercial Ni steam reforming catalysts have also been widely used during the last decades for tar conversion downstream the gasifier bed. Most of them were designed to be used in a fixed bed [10]. They showed activity for tar destruction. Besides complete reforming of methane water-gas shift activity was observed which allowed to adjust the  $H_2/CO$  ratio of the product gas. Nevertheless, they required a product gas without particulates despite gasification gases are a high particle-loaded stream [10]. A hot gas filter would be then needed upstream of the catalytic bed, but the possibility of pore blocking in the filter due to thermal tar conversion was also a potential problem. In this case, the use of catalytic filters would be more advisable [11]. Catalytic filters allow integrating in a one-step cleaning process removal of particles and tar abatement at high temperature. Moreover, catalytic filter candles can be directly integrated into the freeboard of a fluidized bed biomass gasifier called the UNIQUE gasifier concept [12].

In the last years, the performance of these hot gas catalytic filters has been evaluated showing a very good tar and methane reforming activity. Different filter configurations have been tested [13–20]. This paper is focused on fixed bed catalytic filter candles, which consist of a porous inner tube fixed at the head of the filter candle to allow the integration of a catalyst bed. This type of catalytic filter presents the highest potential to provide high catalytic capacity [16], mainly due to two reasons: the possibility to integrate a high amount of catalyst material in the hollow cylindrical space of the filter candle and the possibility to integrate different types of tar-specific reforming catalysts. Nacken et al. [16] evaluated different tar reforming catalytic systems to be integrated in a filter element of the type DIA-SCHUMALITH®. Calcined dolomite,  $CaO-Al_2O_3$  and  $MgO$  were used as catalyst support and different NiO loadings were evaluated. The authors found an important effect of the structural and chemical properties of the support material on the catalytic properties for tar reforming. After testing with naphthalene as model tar compound, they selected an integrated  $MgO$  supported Ni catalyst (6 wt.% NiO loading) to be further evaluated in a bench-scale fluidized bed biomass gasification plant, operating at atmospheric pressure and temperature within the range 800–820 °C [13]. The experimental tests were performed using a segment of a full industrial size filter candle placed in the freeboard of the gasifier, which was a bubbling fluidized bed. Crushed almond shells were utilized as the biomass feedstock. Notable improvements in gas quality when using this type of catalytic filter candle were reported. Hydrogen yield was increased and tar content in the gas was reduced. The main compounds found in the tar were toluene and naphthalene. Pressure drop measurements were carried out with time and they increased with time until a plateau was approached after 22 h of continuous operation.

In the present work, a Fe/olivine guard bed followed by a hot catalytic filter at the outlet of the biomass gasifier has been used for tar abatement. Therefore, the catalytic filter was tested with

**Table 1**

Proximate and ultimate analysis of pine wood (a.r.).

Composition (wt.%)	
Moisture	6.3
Ash	1.1
Volatiles	77.2
Fixed carbon	15.4
C	46.6
H	6.0
N	0.2
S	0.004
Cl	0.002
High heating value (kJ/kg)	18235

real biomass tar generated *in situ* in a DFBBG which adds value to the results obtained. Moreover, the evaluation of the influence of different operational parameters on the filter performance was considered. The tar amount and composition at the inlet of the catalytic filter as well as the face velocity were varied and their effect on tar conversion studied.

## 2. Experimental

### 2.1. Bed material and biomass

Fe/olivine is used as bed material in the fluidized bed gasifier with a particle size in the range 0.1–0.25 mm. Details about the characteristics of this material can be found elsewhere and only a brief information is given here [9]. The Fe/olivine was prepared by impregnation so that the final iron percentage in the olivine was 16%. The biomass feedstock used in this work was pine wood with an average particle size of 0.5–2.0 mm. Table 1 shows the proximate and ultimate analysis of biomass as received (a.r.).

### 2.2. Dual fluidized bed gasification plant

The catalytic filter for tar abatement has been tested with biomass tar produced *in situ* in a bench scale dual fluidized bed gasification plant located at ICB-CSIC. Details about the configuration of this unit can be found elsewhere [9]. Fig. 1 shows a scheme of the gasification plant. The gasifier was a bubbling fluidized bed where biomass was fed in the bed and gasified with steam. Solids exiting the gasifier flowed through a fluidized bed acting as a loop seal to avoid mixing the atmospheres in the gasifier and the combustor. In the combustor, the ungasified char was burnt. The hot solids were transported along a riser, collected by a cyclone and then kept in a solid reservoir which also acted as loop seal. The solid flow returning to the gasifier was controlled with a solid valve. Gas product streams were connected to on-line gas analyzers which determined  $CO$ ,  $CO_2$ ,  $CH_4$ ,  $O_2$  and  $H_2$ . In some specific experiments, off-line gas analyses were carried out in a gas chromatograph (HP 5890) fitted with a Porapack N column to analyze the presence of  $C_1$ – $C_3$  hydrocarbons in the gas outlet stream of the gasifier.

In order to test the effect of the catalytic filter elements in tar reduction, a new reactor and furnace were located downstream the gasifier prior to the tar measurement, as it is shown in Fig. 1. The filter was placed inside this new reactor and then heated by the furnace which allowed controlling the temperature inside the filter. It was possible to by-pass the catalytic filter in order to determine the tar content at the inlet of the catalytic filter.

### 2.3. Catalytic filters

A catalytic filter with dimension  $70 \times 50 \times 30 \times 16$  has been tested in the present work. It was prepared by Pall Filtersystems GmbH from a commercial hot gas filter candle of the type DIA-

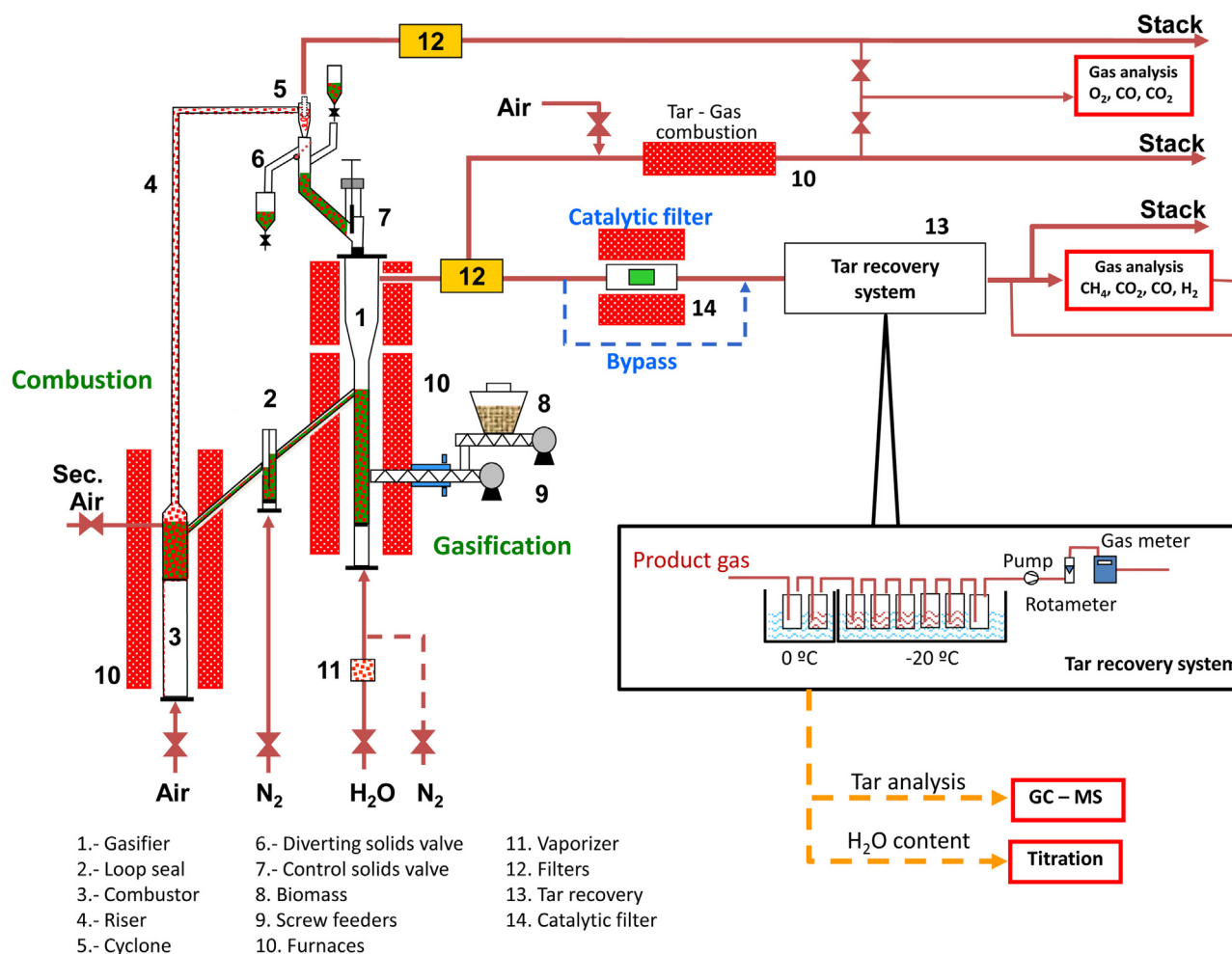


Fig. 1. Scheme of the bench-scale gasification plant at ICB-CSIC.

SCHUMALITH® with a particle separation efficiency of 99.999%. The fixed bed catalyst in the catalytic filter was manufactured by incipient wet impregnation of MgO grains of a particle size between 0.1–0.3 mm using a nickel nitrate hexahydrate solution to obtain a NiO loading of 6 wt.% [16]. In the experiments, only a 21 mm-height segment from the industrial filter candle was used, as it was considered representative on a small scale for the real candle filter in terms of the target face velocity. The segment was covered with ceramic caps at the bottom and upper part of the filter as it is shown in Fig. 2. As mentioned before, the catalytic filter segment was located inside a reactor and a furnace to perfectly control the temperature inside the filter. Fig. 3(A) shows a scheme of the furnace and the location of the reactor inside, as well as the gas path through the filter inside the reactor. Fig. 3(B) shows some photographs of the experimental device used in the experiments. The filter was cleaned with a counter current nitrogen pulse after finishing every experiment.

#### 2.4. Tar sampling and analysis

An off-line method for the tar sampling and analysis based on the European Tar Protocol has been used [21] and was described in detail in a previous paper from the authors [9]. Moisture and tar were collected by a series of eight impinger bottles filled with isopropanol. A cotton filter for further tar capture was placed after the last impinger. The total volumen of dry gas flowed in each measurement was  $\approx 60 I_N$ . The content of the impingers was mixed and characterized off line. The water content of the samples was

determined using the Karl-Fischer titration method (CRISON Titromatic KF1S). The concentration of the different tar compounds was measured in a gas chromatograph (GC Agilent 7890A) coupled with a mass spectrometer (MS Agilent 5975C). The GC was fitted with a capillary column (HP-5) and a flame ionization detector.

#### 2.5. Experimental plan

Table 2 shows a summary of the tests carried out to analyze the performance of the fixed bed catalytic filter. Each test normally corresponds to one-day operation (about 5–6 h at steady state). The operation procedure started with a reference test always performed after reaching steady state. Tars produced in the gasifier were then determined by-passing the catalytic filter. This tar composition corresponds to the inlet composition at the entrance of the catalytic filter. Once the reference tar composition was obtained, the outlet gas from the gasifier was passed through the catalytic filter to reform the tars. The clean gas was sent to the on-line gas analysers. These data correspond to the outlet conditions of the filter, which are compared with the reference test data to evaluate the behaviour of the filter at the different operating conditions. The temperature of the catalytic filter was always maintained at 800 °C, according to the recommendation made by the supplier.

Tests in Table 2 have been organized as they were carried out in order to analyze the possible filter deactivation with time. Moreover, Table 2 includes the values for face velocity ( $u$ ), space velocity in normal conditions (GHSV) and the cumulative operation time





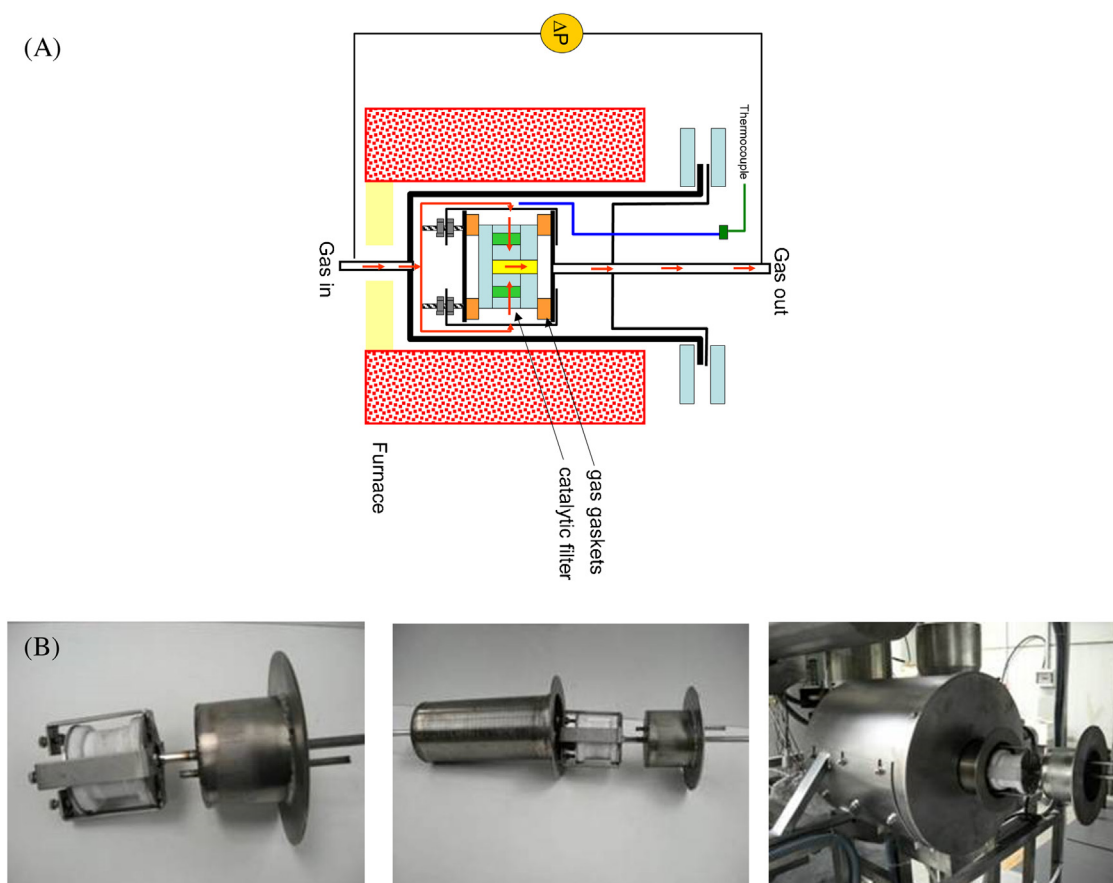


Fig. 3. (A) Catalytic filter located inside the furnace, (B) catalytic filter, reactor and furnace.

### 3. Results and discussion

#### 3.1. Effect of gasification temperature

##### 3.1.1. Tar conversion and composition

Fig. 4 shows the effect of the gasification temperature on the amount of tar found at the inlet of the catalytic filter and in the tar conversion in the filter. Typical values of tar content for fluidized bed gasifiers are in the order of  $10 \text{ g/Nm}^3$  [22]. It can be observed that an increase in the gasification temperature produces an important decrease in the tar content for the reference tests, i.e. without using catalytic filter. At  $750^\circ\text{C}$ , about  $5.7 \text{ g/Nm}^3$  tar were measured while the amount of tar in the gasification gas decreased to  $2.6 \text{ g/Nm}^3$  at  $850^\circ\text{C}$ . An important reduction in the tar obtained using the catalytic filter was observed, with tar conversions about 75% and a final tar content in the gas stream after the catalytic filter about  $0.6 \text{ g/Nm}^3$  at  $850^\circ\text{C}$ . These results are similar to those obtained with the same Ni-based filter candle tested in a bubbling fluidized bed gasifier by Rapagnà et al. [13]. In that case, the biomass feedstock used was crushed almond shells. The biomass was delivered from the top of the reactor by a continuous feeder. The gases leaving the bubbling fluidized bed were condensed and analysed to determine tar and gas composition. At a gasification temperature around  $800^\circ\text{C}$ ,  $\text{H}_2\text{O}$ :biomass (w/b) ratio set to one and face velocities between 60 and  $100 \text{ m/h}$ , the tar conversion values obtained in these experiments were about 60–70%.

The effect of the catalytic filter on tar reduction was also visually observed through the colour of the tars recovered in the impingers. Fig. 5 shows an example of the tars recovered at the inlet and outlet of the catalytic filter. It was observed, that the use of the catalytic filter produced an important change in the colour of the liquid prod-

ucts, which it is an indication of the presence of lower tar amount. As it can be observed, almost transparent and colourless liquids were obtained.

More than the quantity of tar it is interesting to know its composition as it is linked to the properties of tar such as water solubility or dew point. The effect of the catalytic filter on the tar composition at different temperatures and operating with a face velocity of  $60 \text{ m/h}$  is shown in Fig. 6. Naphthalene, indene, styrene, biphenyl and phenanthrene were the main tar compounds in the raw gas using Fe/olivine in the fluidized bed. According to what it is observed in Fig. 6, conversions between 70 and 100% were reached in the catalytic filter for all the tar compounds detected except naphthalene at the two temperatures presented. In the case of naphthalene, conversion was lower, around 50–60%, confirming that naphthalene was the most stable molecule [9]. At  $750^\circ\text{C}$ , the tar characterization carried out showed that the most important compound after the catalytic filter was naphthalene followed in minor amount by indene and biphenyl. At  $850^\circ\text{C}$ , naphthalene was the unique compound existent in the tar.

##### 3.1.2. Syngas composition

Table 3 summarizes the operating conditions and main results obtained in the tests performed in the present work at different gasification temperatures. In this case, syngas composition at the inlet and outlet of the catalytic filter was determined. An increase of the gasification temperature produced small changes in the raw gas composition: the CO decreased and the  $\text{CO}_2$  increased in a small amount, meanwhile the  $\text{H}_2$  and  $\text{CH}_4$  remain almost constant. Fig. 7 compared the composition (dry  $\text{N}_2$  free) of the syngas at the inlet and outlet of the catalytic filter using a face velocity close to  $60 \text{ m/h}$ . An important increase in the  $\text{H}_2$  percentage was observed

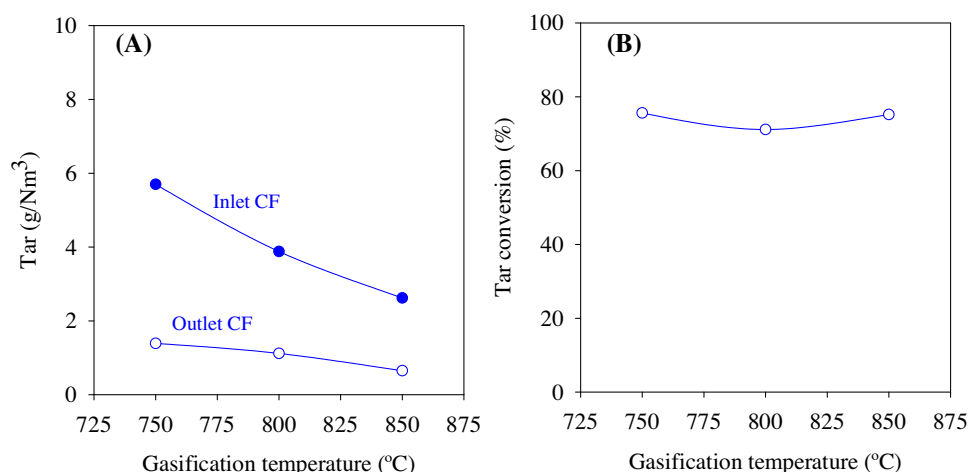


Fig. 4. Effect of the gasification temperature on the tar content and conversion before and after the catalytic filter at face velocity = 60 m/h.

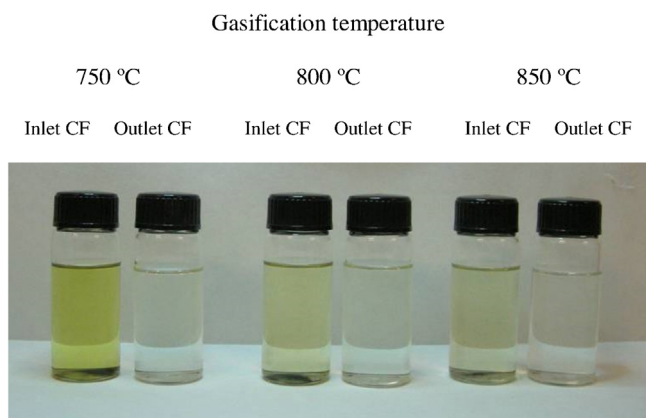
Table 3

Operating conditions and experimental results of the tests with the catalytic filter.

Bed solid Catalytic filter	Fe/Olivine Inlet	Fe/Olivine Outlet	Fe/Olivine Outlet	Fe/Olivine Inlet	Fe/Olivine Outlet	Fe/Olivine Outlet	Fe/Olivine Inlet	Fe/Olivine Outlet	Fe/Olivine Outlet
Filter temperature (°C)		800	800		800	800		800	800
Filter gas velocity (m/h)		74	60		75	67		74	62
Filter pressure drop (mbar)		18	15		17	16		25	11
Gas flow (l <sub>N</sub> /h)		87	71		89	79		87	73
Temperatures (°C)									
Gasifier	750	750	750	800	800	800	850	850	850
Gas. freeboard	800	800	800	800	800	800	800	800	800
Combustor	900	900	900	900	900	900	900	900	900
Operating conditions									
Biomass (g/h)	261	261	261	258	258	258	241	241	241
H <sub>2</sub> O/biomass dry (g/g)	0.52	0.52	0.52	0.52	0.52	0.52	0.57	0.57	0.57
Gas composition (vol%, N <sub>2</sub> free, dry basis)									
Gasifier									
CO	22.9	18.9	18.5	21.7	18.9	19.1	18.7	18.2	18.3
CO <sub>2</sub>	35.4	32.5	32.6	37.8	33.0	32.4	41.9	35.2	34.4
H <sub>2</sub>	27.6	37.8	38.8	27.2	37.1	37.6	26.7	35.5	36.3
CH <sub>4</sub>	9.9	8.3	8.3	9.2	7.7	7.5	8.8	7.7	7.7
C <sub>2</sub> H <sub>4</sub>	3.6	1.5	1.4	3.3	2.8	2.7	3.2	2.8	2.8
C <sub>2</sub> H <sub>6</sub>	0.4	0.3	0.3	0.4	0.3	0.3	0.4	0.3	0.3
C <sub>3</sub> H <sub>8</sub>	0.3	0.7	0.0	0.3	0.2	0.2	0.3	0.2	0.2
Combustor									
O <sub>2</sub>	14.5	14.3	14.7	15.5	15.8	15.6	15.4	15.4	15.8
CO <sub>2</sub>	3.8	3.9	3.6	2.7	2.5	2.6	1.8	1.8	1.6
Tar (g/Nm <sup>3</sup> dry)	5.70	1.65	1.39	3.88	1.42	1.12	2.62	0.87	0.65
H <sub>2</sub> O content (vol.%)	30.6	30.2	29.5	42.9	32.3	34.1	41.4	31.1	32.4
Tar conversion (%)	–	71	75	–	63	71	–	66	75
Tar composition (g/Nm <sup>3</sup> dry)									
Styrene	0.33	0.00	0.00	0.21	0.00	0.00	0.14	0.00	0.00
Phenol	0.17	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Benzofuran	0.24	0.00	0.00	0.23	0.00	0.00	0.00	0.00	0.00
Indene	1.45	0.15	0.10	0.96	0.06	0.00	0.39	0.00	0.00
Naphtalene	2.41	1.29	1.16	1.94	1.27	1.11	1.77	0.87	0.65
Biphenylen	0.51	0.08	0.06	0.24	0.04	0.00	0.16	0.00	0.00
Fluorene	0.13	0.00	0.00	0.04	0.00	0.00	0.00	0.00	0.00
Phenanthrene	0.28	0.05	0.04	0.15	0.04	0.00	0.11	0.00	0.00
Anthracene	0.02	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00
Fluoranthene	0.07	0.04	0.02	0.05	0.00	0.01	0.03	0.00	0.00
Pyrene	0.07	0.03	0.01	0.05	0.00	0.00	0.02	0.00	0.00
TOTAL	5.68	1.64	1.39	3.89	1.41	1.12	2.62	0.87	0.65

when using the catalytic filter as well as a decrease in the other syngas components (CO, CO<sub>2</sub> and CH<sub>4</sub>), as a consequence of the reforming of CH<sub>4</sub> or higher hydrocarbons that takes place inside the filter. Regarding the mechanism for tar conversion and hydrocarbon reforming in the catalytic filter different overlapping processes can be considered. It has been reported that only the char cake

formed when non-catalytic filter elements are used has an effect on the tar and gas composition of the gasification gas [23]. The hydrogen content increased and heavier tar species were converted to lighter compounds. In fact, Simeone et al. [23] reported an increase of around 10% in hydrogen concentration at the outlet of a non-



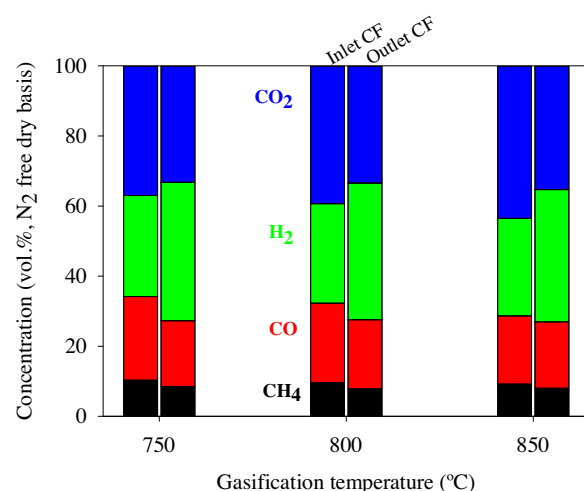
**Fig. 5.** Effect of the catalytic filter (CF) on the tar recovered in the impingers at different gasification temperatures.

catalytic filter operating at 800 °C in experiments with different biomass feedstocks.

The high temperatures and the long residence time on the filter seem to be responsible of these thermal tar reactions, although the biomass char that is retained by the filter is also thought to catalyse the conversion of tar and methane [24,25]. The catalytic effect of char particles would be enhanced due to the improved contact between char particles and product gas. Nevertheless, when catalytic filters are used, the prevailing mechanism for tar conversion and hydrogen production is linked to the catalytic reactions taking place in the filter more than to the char catalytic activity [24].

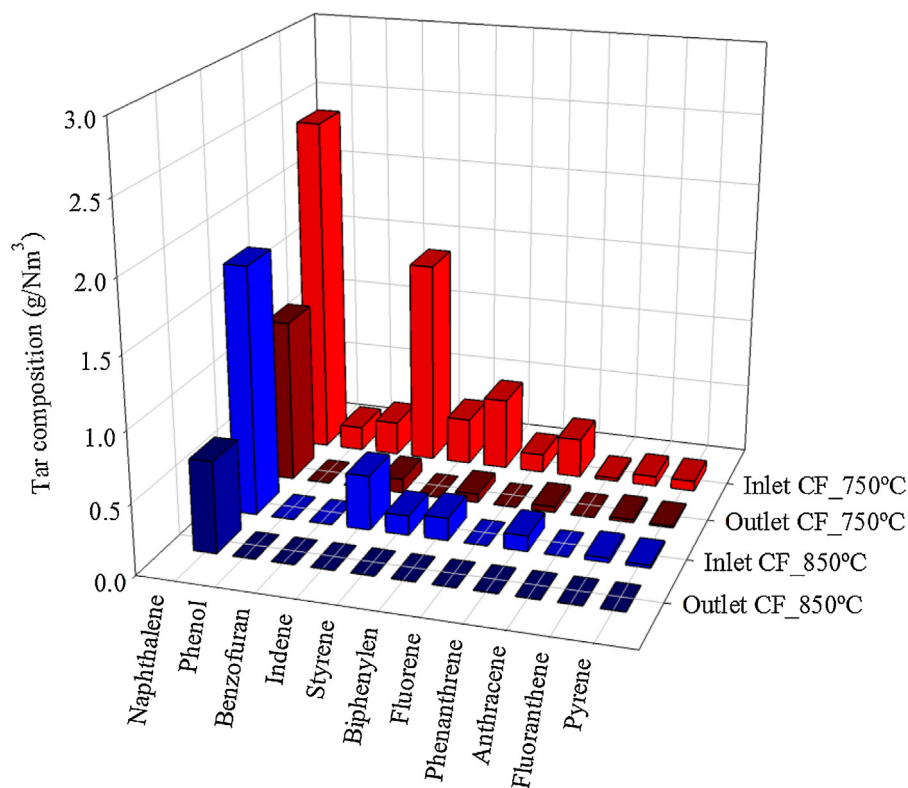
### 3.1.3. Analysis of $C_2$ – $C_3$ hydrocarbons in syngas

To analyze the existence of higher hydrocarbons ( $C_2$ – $C_3$ ) in the gaseous stream of the gasifier, some gas samples were collected in the experiments carried out and analysed by off-line gas



**Fig. 7.** Effect of the catalytic filter (CF) on syngas composition at different gasification temperatures. Face velocity = 60 m/h.

chromatography. Similar gas composition was obtained for both methods for  $CO$ ,  $CO_2$ ,  $H_2$  and  $CH_4$ . Some minor amounts of ethylene (1–4%), ethane (<0.5%) and propane (<0.5%) were measured at the outlet stream of the gasifier. The effect of the catalytic filter on these hydrocarbons is more important with ethylene than with the other compounds, although a reduction in  $C_2$ – $C_3$  concentration was always observed at the outlet of the catalytic filter. About 60% of ethylene reduction was measured in the tests with the catalytic filter.



**Fig. 6.** Effect of catalytic filter (CF) on tar composition at  $T_{\text{gasif.}}=750$  °C and 850 °C. Face velocity = 60 m/h.

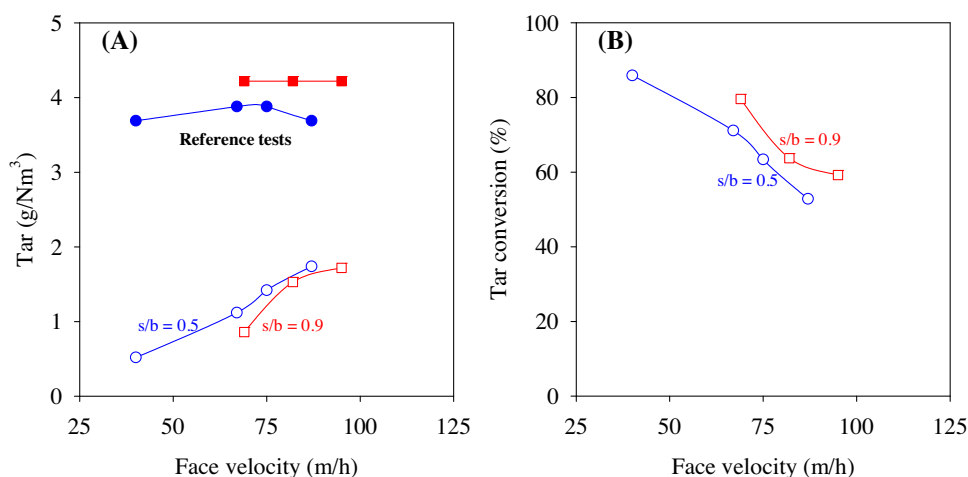


Fig. 8. Effect of the face velocity on the tar content at the inlet and outlet of the catalytic filter (CF) and on tar conversion at different steam/biomass ratios.  $T_{\text{gasif.}}=800^{\circ}\text{C}$ .

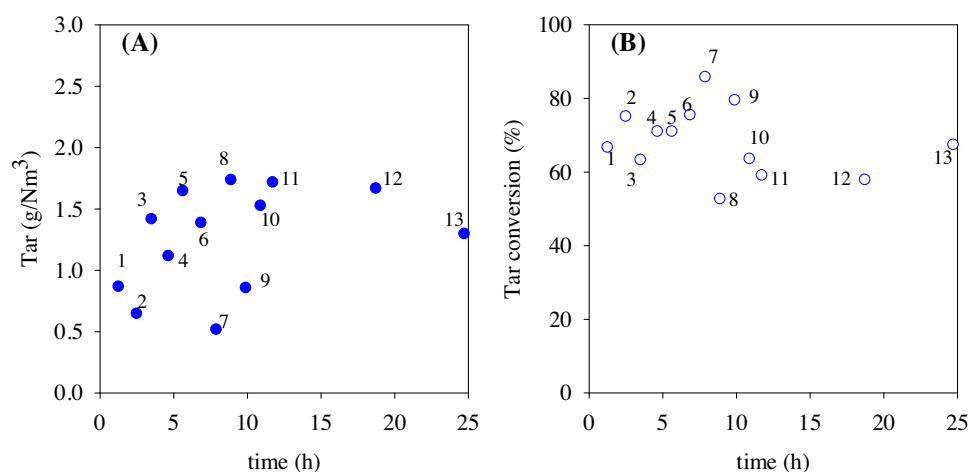


Fig. 9. Tar content and tar conversion evolution with time for the fixed bed catalytic filter.

### 3.2. Effect of gas velocity through the filter

The selection of an adequate value for the face velocity is of interest regarding the economics of the gasification plant. Higher face velocities can reduce the number of filter candles used and therefore the associated cost. Reducing costs is especially important for small to medium scale gasification plants. The use of fewer catalytic filter candles implies a simplification and intensification of the biomass gasification process as well as an increase in the efficiency of biomass conversion. Nevertheless and in order to reduce the number of filter candles used, other aspects should also be considered together with the face velocity, as it is the case of the amount of catalyst in the catalytic filter and the total weight of the filter candle.

The usual values of face velocities used with non-catalytic filters oscillate between 70 and 120 m/h [16]. In contrast, in the case of catalytic filters, not only the face velocity but also the space velocity should be adequate for the catalytic tar reforming reaction to take place.

As it was previously mentioned in the description of the experimental plan, the fixed bed catalytic filter was used in experiments with different gas face velocities ranging from 40 to 90 m/h. Results for experiments performed with the tar produced during biomass gasification at  $800^{\circ}\text{C}$  are presented in Fig. 8. In this range of face velocities tested, it can be observed that tar conversion decreased

when the gas velocity increased. This fact can be mainly attributed to the lower residence time of the gas inside the catalytic filter. As it can be observed in Fig. 8, the same trend of decreasing tar conversion at higher face velocities was found working with two different  $\text{H}_2\text{O}$  to dry biomass ratios, i.e. 0.5 and 0.9. Nevertheless, the values of tar conversion were higher for the highest  $\text{H}_2\text{O}$  to dry biomass ratio. In the case of non-catalytic filters, several authors have previously established that an increase in residence time on the filter enables the continuation of thermal tar reactions [23,25]. With catalytic filters, in experiments using naphthalene as model tar compound, Nacken et al. [16] found that doubling the filtration velocity from 90 to 180 m/h a decrease in the catalytic activity of two different Ni-based catalytic filters was detected, also corroborating the present results. The same authors also reported the same trend in further works with fixed bed and other configurations of catalytic filters [26]. In that work, Nacken et al. [26] reported space velocity values between 3120 and  $4160\text{ h}^{-1}$  for the conversion of naphthalene in a fixed bed catalytic filter which are also similar to those found in the present work and summarized in Table 2 for biomass tar conversion. On the other hand, the changes in face velocity did not significantly affect the syngas composition at the outlet of the fixed bed catalytic filter at any of the steam/biomass ratios tested. However, the increase in the face velocity did affect the composition of the tar at the outlet of the catalytic filter. Using a steam/biomass ratio equal to 0.5, only naphthalene was present at the outlet of



the filter at the lowest velocity tested (40 m/h). As the face velocity increased, traces of indene, biphenyl and phenanthrene could be observed. At the highest face velocity (90 m/h), also low amounts of fluoranthene and pyrene were present. These results in tar composition with the increase of face velocity were also obtained in the experiments with the highest steam/biomass ratio, i.e. 0.9, although in this case the ratio between the amount of naphthalene and the rest of tar compounds was larger.

Considering all the above results, a compromise between face velocity and tar conversion should be reached in order to optimize filter candle operating conditions. In this optimization, other aspects such as the pressure drop through the catalytic filter should be considered. The pressure drop through the catalytic filter in the experiments at different face velocities and steam/biomass ratios increased with the value of face velocity and oscillated between 9 and 32 mbar, which can be considered as normal values for this type of catalytic filters.

### 3.3. Long run experiments

The performance of the catalytic filter with time should be evaluated to test the catalytic activity of the filter after several hours of continuous operation. Fig. 9 presents the evolution of tar content and tar conversion with time obtained during the whole experimentation carried out with the fixed bed catalytic filter. All the experimental data in Table 2 corresponding to the different operating conditions was shown and the number of experiment was indicated on the corresponding point in the graph. Note that the dispersion in Fig. 9 can be attributed to the different experimental conditions used for each point plotted. After 24 h of continuous operation of the filter, the catalytic activity was maintained. Tar contents lower than 2 g/Nm<sup>3</sup> are observed and tar conversion around 75% can be obtained with this catalytic filter. According to the values found in literature [6], this tar content would allow the gasification gas generated to be used in gas engines or turbines. However, despite the significant tar reduction obtained, the tar content would still be too high for the gas to be used in fuel cells or in the production of chemicals. In order to further decrease the tar content, some modifications in the configuration of the catalytic filter should be undertaken.

## 4. Conclusions

A fixed bed catalytic filter for hot conditioning of biomass gasification gas has been tested in experiments in a dual fluidized bed gasifier (DFBG). This novel tar abatement technology has been evaluated using real biomass tar produced in this continuous unit. Several parameters affecting the performance of the catalytic filter were systematically analysed, such as tar amount and composition (produced at different gasification temperatures and steam/biomass ratios) and face velocity in the filter.

The amount of tar at the inlet of the catalytic filter was varied by changing the gasification temperature in the range 750–850 °C. The higher the gasification temperature the lower the amount of tar in the gasifier outlet was. In experiments with different tar concentrations at the inlet, the catalytic filter demonstrated effectiveness in tar reduction and conversions around 75% were reached. In the experiment at the highest gasification temperature (850 °C), the total tar amount at the outlet of the catalytic filter was 0.65 g/Nm<sup>3</sup>. The only tar compound present in this gas was naphthalene, as it is the most resistant tar compound of those detected.

High face velocities (90 m/h) in the catalytic filter led to a decrease in tar conversion as the residence time of the gas inside the catalytic filter was decreased. Therefore this parameter should be optimized considering also the solid filtering needs in the gasifier unit.

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## References

- [1] G. Xu, T. Murakami, T. Suda, Y. Matsuzawa, H. Tani, *Ind. Eng. Chem. Res.* 45 (2006) 2281–2286.
- [2] M. Bolhär-Nordenkamp, R. Rauch, K. Bosch, C. Aichernig, H. Hofbauer, Biomass CHP plant Güssing—using gasification for power generation, *International Conference on Biomass Utilisation* (2002).
- [3] M.C. Seemann, H. Thunman, The new Chalmers research-gasifier, *International Conference on Polygeneration Strategies* (2009).
- [4] T.A. Milne, R.J. Evans, N. Abatzoglou, Biomass Gasifier Tars: Their Nature, Formation and Conversion, National Renewable Energy Laboratory (NREL) Technical Report Colorado, 1998.
- [5] K. Maniatis, A.A.C.M. Beenackers, *Biomass Bioenergy* 18 (2000) 1–4.
- [6] H.A.M. Knoef, Handbook Biomass Gasification, BTG Biomass Technology Group, Enschede, The Netherlands, 2005.
- [7] W. Torres, S.S. Pansare, J.G. Goodwin Jr., *Cat. Rev. Sci. Eng.* 49 (2007) 407–456.
- [8] M. Virginie, C. Courson, D. Niznansky, N. Chaoui, A. Kiennemann, *Appl. Catal. B: Environ.* 101 (2010) 90–100.
- [9] M. Virginie, J. Adánez, C. Courson, L.F. De Diego, F. García-Labiano, D. Niznansky, A. Kiennemann, P. Gayán, A. Abad, *Appl. Catal. B: Environ.* 121–122 (2012) 214–222.
- [10] J. Corella, J.M. Toledo, R. Padilla, *Ind. Eng. Chem. Res.* 43 (2004) 2433–2445.
- [11] M.P. Duduković, F. Larachi, P.L. Mills, *Cat. Rev. Sci. Eng.* 44 (2002) 123–246.
- [12] S. Heidenreich, P.U. Foscolo, *Prog. Energy Combust. Sci.* 46 (2015) 72–95.
- [13] S. Rapagnà, K. Gallucci, M. di Marcello, M. Matt, M. Nacken, S. Heidenreich, P.U. Foscolo, *Bioresour. Technol.* 101 (2010) 7123–7130.
- [14] K. Engelen, Y. Zhang, D.J. Draelants, G.V. Baron, *Chem. Eng. Sci.* 58 (2003) 665–670.
- [15] L. Ma, H. Verelst, G.V. Baron, *Catal. Today* 105 (2005) 729–734.
- [16] M. Nacken, M. Lina, K. Engelen, S. Heidenreich, G.V. Baron, *Ind. Eng. Chem. Res.* 46 (2007) 1945–1951.
- [17] M. Nacken, L. Ma, S. Heidenreich, G.V. Baron, *Appl. Catal. B: Environ.* 88 (2009) 292–298.
- [18] S. Rapagnà, K. Gallucci, M.D. Marcello, P.U. Foscolo, M. Nacken, S. Heidenreich, *Energy Fuels* 23 (2009) 3804–3809.
- [19] M. Nacken, L. Ma, S. Heidenreich, F. Verpoort, G.V. Baron, *Appl. Catal. B: Environ.* 125 (2012) 111–119.
- [20] A. D'Orazio, S. Rapagnà, P.U. Foscolo, K. Gallucci, M. Nacken, S. Heidenreich, A. Di Carlo, A. Dell'Era, *Int. J. Hydrogen Energy* 40 (2015) 7282–7290.
- [21] P. Simell, P. Ståhlberg, E. Kurkela, J. Albrecht, S. Deutsch, K. Sjöström, *Biomass Bioenergy* 18 (2000) 19–38.
- [22] L.P.L.M. Rabou, R.W.R. Zwart, B.J. Vreugdenhil, L. Bos, *Energy Fuels* 23 (2009) 6189–6198.
- [23] E. Simeone, M. Siedlecki, M. Nacken, S. Heidenreich, W. De Jong, *Fuel* 108 (2013) 99–111.
- [24] S. Rapagnà, A. D'Orazio, K. Gallucci, P.U. Foscolo, M. Nacken, S. Heidenreich, Hydrogen rich gas from catalytic steam gasification of biomass in a fluidized bed containing catalytic filters, *Chem. Eng. Trans.* (2014) 157–162.
- [25] S. Tuomi, E. Kurkela, P. Simell, M. Reinikainen, *Fuel* 139 (2014) 220–231.
- [26] M. Nacken, L. Ma, S. Heidenreich, G.V. Baron, *Ind. Eng. Chem. Res.* 49 (2010) 5536–5542.